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13. ABSTRACT (MAX 200 WORDS): THE RATE OF NUCLEOPHILIC SUBSTITUTION AT THE PHOSPHORUS CENTRE OF DIALKYL METHYLPHOSPHONATES BY METHOXIDE AND ETHOXIDE HAS BEEN STUDIED TO INVESTIGATE THE POSSIBLE INVOLVEMENT OF HEXACOORDINATED PHOSPHORUS SPECIES IN THIS REACTION. FOR ALKOXIDE CONCENTRATIONS LESS THAN CA. 1.5M THE RATE INCREASES WITH THE SQUARE OF ALKOXIDE CONCENTRATION. HOWEVER, CONSIDERATION OF THE ACTIVITY OF ALKOXIDES, REPRESENTED BY AN APPROPRIATE ACIDITY FUNCTION, REVEALS THAT ONLY ONE EQUIVALENT OF ALKOXIDE IS INVOLVED IN THE RATE-DETERMINING STEP. THUS, THERE IS NO REQUIREMENT TO INVOKE THE INTERMEDIACY OF HEXACOORDINATED SPECIES IN THE REACTION PATHWAY.					
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Investigation of the Reaction Order for Nucleophilic Substitution of Dialkyl Methylphosphonates by Alkoxides

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Abstract

The rate of nucleophilic substitution at the phosphorus centre of dialkyl methylphosphonates by methoxide and ethoxide has been studied to investigate the possible involvement of hexacoordinated phosphorus species in this reaction. For alkoxide concentrations less than ca. 1.5 M the rate increases with the square of alkoxide concentration. However, consideration of the activity of the alkoxides, represented by an appropriate acidity function, reveals that only one equivalent of alkoxide is involved in the rate-determining step. Thus, there is no requirement to invoke the intermediacy of a hexacoordinated species in the reaction pathway. © 1992 John Wiley & Sons, Inc.

Introduction

Nucleophilic substitution at phosphorus has been extensively studied and the role of pentacoordinate species, as either intermediates or transition states in the reaction pathway, is firmly established [1]. According to the accepted mechanism, substitution is first order with respect to the nucleophile under most circumstances. However, the potential for the involvement of hexacoordinate species in substitution of phosphate esters has received attention [2–7], being strongly supported at one time [3]. For the hydrolysis of methyl ethylene phosphate the proportion of exocyclic cleavage increases with hydroxide concentration, indicating that the mechanism for formation of this product has a higher order dependency on hydroxide than does endocyclic cleavage. The change in product distribution may be interpreted as evidence of the intermediacy of a hexacoordinate species [2]. Support for the proposal that the role of the second equivalent of hydroxide is to add to the initially formed pentacoordinate intermediate to form a hexacoordinate species may be elicited from mechanistic studies of the base catalysed hydrolysis of stable pentacoordinated phosphorus compounds [8–12], and also the isolation of stable hexacoordinate phosphorus compounds [13,14]. An alternate (favored) rationalization offered for the role of the second equivalent of base in the hydrolysis of methyl ethylene phosphate was that it deprotonates an apical hydroxyl ligand in a pentavalent intermediate [2]. An analysis of the products obtained when the reaction is performed in ^{18}O labelled water has demonstrated that hydrolysis in strongly alkaline solutions does not proceed via a hexacoordinated intermediate [7]. More recently, the involvement of a hexacoordinated species as a transition state in the reaction pathway has been excluded [15].

We have observed that the reaction of dialkyl alkylphosphonates in diethylene triamine/ethylene glycol monomethyl ether/sodium hydroxide exhibits a high order dependency (ca. 2) on the hydroxide concentration [16]. The nucleophile in this reaction is the alkoxide rather than hydroxide, as evident from the initially formed product. The high order dependency upon alkoxide concentration suggests that this reaction may involve a hexacoordinated species. Unlike the hydrolysis of methyl ethylene phosphate, the pentacoordinated intermediate formed by addition of alkoxide to a dialkyl alkyl phosphonate does not possess a hydroxyl ligand that may be deprotonated by a second equivalent of base. The effect of alkoxide concentration on the rate of reaction of alkoxides with phosphorus esters has not previously been fully explored, and the apparent second order dependence on alkoxide concentration may have significant mechanistic implications. A clear demonstration of nucleophilic substitution at phosphorus that is second order with respect to the nucleophile, where deprotonation of the pentacoordinated intermediate is not possible would provide support for the involvement of hexacoordinated species in the reaction. In this work we investigate the reaction of dialkyl methylphosphonates with alkoxides in the corresponding alcohol solvent, to determine the order of the reaction.

Experimental

Dimethyl methylphosphonate (Aldrich, >99%) and redistilled commercial samples of diethyl methylphosphonate (DEMP), ethyl benzoate and methyl benzoate were dried over 4Å molecular sieves prior to use. The DEMP was shown to contain ca. 8 mol percent diethyl ethylphosphonate by ^{31}P NMR. Stock solutions of alkoxides were prepared by reaction, under nitrogen, of weighted amounts of sodium metal with absolute ethanol or methanol previously dried by storage over 4Å molecular sieves. The concentration of alkoxide was then determined titrimetrically. Dilution of the stock solutions with the corresponding alcohol provided solutions of varying concentration for the reaction studies.

Reaction of dimethyl methylphosphonate (DMMP) and DEMP with sodium ethoxide or methoxide respectively was monitored by ^{31}P NMR. Alkoxide solution (5 ml) was transferred to a 10 mm o.d. NMR tube and equilibrated at 25°C in a thermostatted water bath or the probe of the NMR spectrometer. The alkoxide/substrate ratio was maintained at ca. 15:1 for ethoxide/DMMP and ca. 30:1 for methoxide/DEMP reactions. ^{31}P spectra were then acquired over the course of the reaction for at least 2 half-lives.

NMR spectra were recorded using a Bruker AM-300 Fourier transform NMR Spectrometer equipped with a B-VT1000 variable temperature accessory which was used to maintain the sample temperature at $25.0 \pm 0.5^\circ\text{C}$ for kinetic experiments. ^{31}P spectra were obtained with inverse gating of ^1H decoupling to suppress the nuclear Overhauser enhancement (0.8 s acquisition time, 10.2 s relaxation delay) and were referenced to external 85% phosphoric acid. The number of transients acquired for each spectrum depended on the rate of reaction, with a minimum of 4 for the fastest reactions. A line broadening of 5 Hz was applied to the spectra during processing. Peak heights for each species observed were assumed to be proportional to concen-

tration. The fraction of the substrate unreacted was then calculated from its contribution to the total concentration of ^{31}P containing compounds in solution. The diethyl ethylphosphonate impurity in the DEMP did not interfere with these calculations as the reactant, product and impurity peaks were all well resolved.

The reaction of ethyl benzoate with sodium methoxide was monitored by GC. The stirred alkoxide solution (5 ml) was equilibrated at 25°C in a glass reaction cell under a dry nitrogen atmosphere before the reaction was initiated by addition of substrate. The methoxide/ethyl benzoate ratio was ca. 30:1 for each reaction. Aliquots (0.5 ml) were periodically removed from the cell and added to 1.0 ml of 1 M HCl to quench the reaction. GC analysis (25 m \times 0.25 mm fused silica BP5 capillary column) of the dichloromethane extract of the quenched sample provided the ratio of substrate to product (methyl benzoate) after correction for the mole response of the FID detector to each compound. The extent of reaction was then determined from this ratio.

The pseudo first-order rate constant (k_{obs}) for each reaction was calculated by fitting the fraction of reactant remaining (P_t) as a function of time (t) to eq. (1) using a least squares procedure which provided values for both k_{obs} and P_0 .

$$(1) \quad P_t = P_0 e^{-k_{\text{obs}} t}$$

Results

The ^{31}P chemical shifts of the reactants and products of the dialkyl methylphosphonate/alkoxide reactions measured in various solvents, and literature values [17] are given in Table I. Although considerable variation of chemical shifts with solvent change is evident, there is no ambiguity in peak assignments. The shifts for DMMP and DEMP in each solvent were obtained from authentic samples of these esters. Ethyl methyl methylphosphonate (EMMP) is the common product from ethanolysis of DMMP and methanolysis of DEMP, and is readily identified in the ^{31}P spectra from the time dependence of its concentration during the alcoholysis reactions (see below). ^{31}P chemical shifts in aqueous hydroxide solution for monoethyl methylphosphonate (MEMP) and monomethyl methylphosphonate (MMMP), prepared by base hydrolysis of the diesters DEMP and DMMP are re-

TABLE I. ^{31}P Chemical shifts of dialkyl and monoalkyl methylphosphonates (δ ppm, 85% H_3PO_4 reference).

Solvent	Chemical Shift				
	DMMP	EMMP	DEMP	MMMP	MEMP
EtOH	35.30				
EtOH/EtO $^-$	34.56	33.15	31.71	25.84	24.41
MeOH			33.48		
MeOH/MeO $^-$	36.12	34.68	33.22	26.84	25.41
H $_2$ O/OH $^-$				29.01	27.54
—	32.3–32.6 a		29.1–30.0 a		28.5 a

a From ref. [17].

ported [18]. The corresponding peaks in the alcohol/alkoxide reaction solutions were identified by observing intensity changes in the ^{31}P spectra of these solutions after separate additions of aqueous solutions of each monoester.

Reaction of DMMP in sodium ethoxide/ethanol initially yields EMMP which further reacts to give DEMP as shown in Figure 1. In addition, a trace (less than 2% of products) of MMMP is formed. Conversion of DMMP to EMMP with excess ethoxide obeys first order kinetics for at least 3 half-lives. Observed pseudo first-order rate constants (k_{obs}) for the reaction, monitored over a range of concentrations are given in Table II. Included in the table are the second order rate constants (k_2) calculated according to Eq. (2), where k_0 is the observed rate when the concentration of alkoxide is zero. A value for k_0 of less than $5 \times 10^{-7} \text{ min}^{-1}$ was estimated for ethanolysis of DMMP since EMMP was not detected by ^{31}P NMR (i.e., less than ca. 0.5%) in an ethanol solution of DMMP maintained at 25°C for 168 h.

$$(2) \quad k_2 = (k_{\text{obs}} - k_0)/[\text{alkoxide}]$$

EMMP is slowly formed when DEMP reacts with sodium methoxide, and in turn reacts with methoxide to form DMMP (Fig. 2). A small amount (less than 4% of products) of MEMP is also formed. MMMP, which cannot be formed directly from DEMP, and therefore has no impact on the rate being determined is also present after long reaction times. Conversion of DEMP to EMMP with excess methoxide is a first order process. Values of k_{obs} and k_2 for the reaction of EMMP with sodium methoxide are given in Table III.

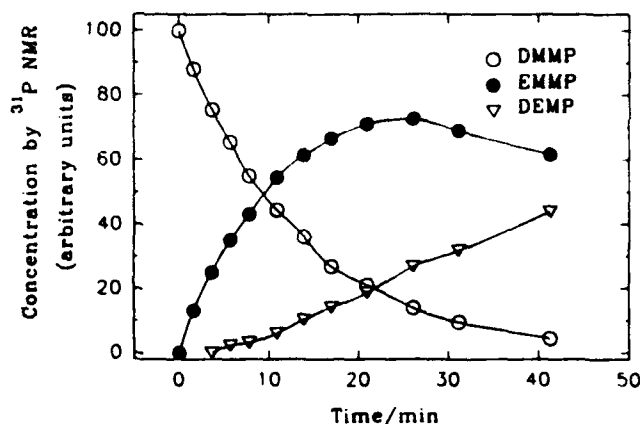


Figure 1. Reactant and product concentrations during the reaction of DMMP (0.090 M) with NaOEt (1.36 M) in ethanol at 25°C.

TABLE II. Rates for reaction of DMMP with sodium ethoxide at 25°C.

[NaOEt]/M	[DMMP]/M	$k_{\text{obs}}/(\text{min}^{-1} \times 10^{-2})$	$k_2/(\text{lt mol}^{-1} \text{ min}^{-1} \times 10^{-2})$
0.68	0.046	1.58 ± 0.02	2.32
0.95	0.063	3.13 ± 0.07	3.29
1.09	0.072	4.35 ± 0.04	3.99
1.22	0.079	5.93 ± 0.06	4.86
1.36	0.090	7.49 ± 0.06	5.51

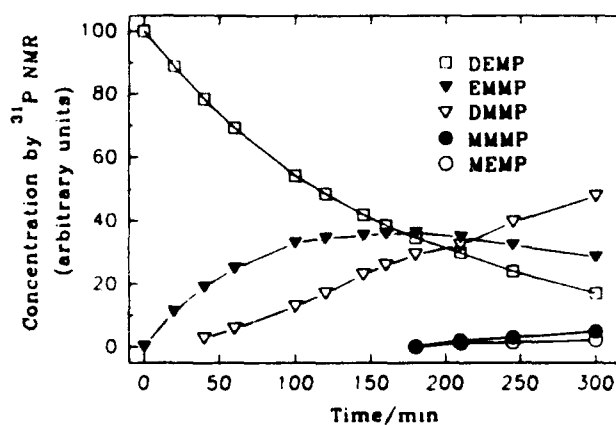


Figure 2. Reactant and product concentrations during the reaction of DEMP (0.068 M) with NaOMe (2.14 M) in methanol at 25°C.

TABLE III. Rates for reaction of DEMP with sodium methoxide at 25°C.

[NaOMe]/M	[DEMP]/M	$k_{\text{obs}}/(\text{min}^{-1} \times 10^{-4})$	$k_2/(\text{lt mol}^{-1} \text{min}^{-1} \times 10^{-4})$
0.38	0.014	1.66 ± 0.04	4.36
0.57	0.021	2.96 ± 0.03	5.19
0.76	0.027	4.85 ± 0.04	6.38
0.96	0.034	6.71 ± 0.1	6.99
1.15	0.041	10.0 ± 0.2	8.69
1.48	0.049	16.2 ± 0.1	10.9
1.93	0.062	38.7 ± 0.2	20.1
2.14	0.068	59.8 ± 0.9	27.9

For this reaction, k_0 was estimated as less than $5 \times 10^{-7} \text{ min}^{-1}$ (less than 0.5% reaction after 168 h at 25°C).

The alcoholysis of ethyl benzoate in sodium methoxide/methanol adhered to pseudo first order kinetics for at least 3 half-lives. Rate data for this reaction are summarized in Table IV.

Discussion

The consistent increases in k_2 with increasing alkoxide concentration for the dialkyl methylphosphonate/alkoxide reactions indicate that these reactions are not first order with respect to alkoxide concentration. However, when k_{obs} is plotted against $[\text{alkoxide}]^2$ good linear correlations are obtained for alkoxide concentrations below ca. 1.5 M (Figs. 3 and 4), suggesting the reactions are second order with respect to alkoxide. The DEMP/methoxide

TABLE IV. Rates for reaction of ethyl benzoate (EB) with sodium methoxide at 25°C.

[NaOMe]/M	[EB]/M	$k_{\text{obs}}/(\text{min}^{-1})$
0.20	0.007	0.056 ± 0.001
0.39	0.014	0.140 ± 0.001
0.59	0.021	0.200 ± 0.008
0.81	0.028	0.325 ± 0.005
1.01	0.035	0.499 ± 0.008

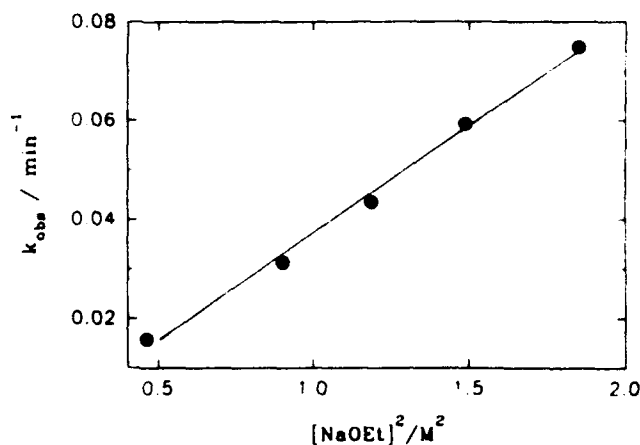


Figure 3. Rate of reaction vs. $[\text{alkoxide}]^2$ for reaction of DMMP with NaOEt (corr. coeff. for least squares fit = 0.997).

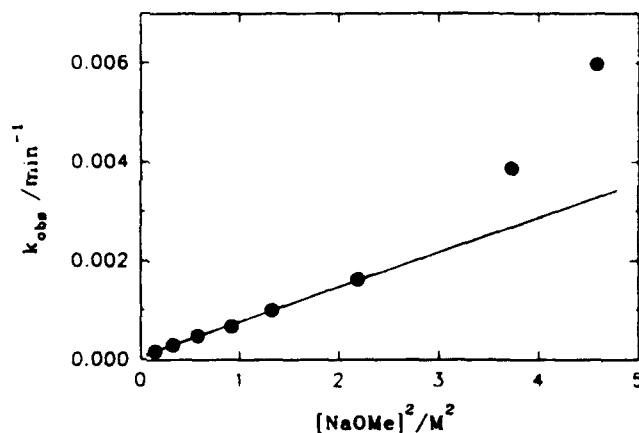


Figure 4. Rate of reaction versus $[\text{alkoxide}]^2$ for reaction of DEMP with NaOMe (least squares line for $[\text{NaOMe}] < 1.5 \text{ M}$, corr. coeff. = 0.999).

reaction was studied at two higher methoxide concentrations, and the reaction rates greatly exceeded the values predicted by the linear correlation evident at the lower concentrations. Thus, it is unclear whether the nucleophilic substitution at phosphorous by alkoxide, exemplified by the reactions under study are second order with respect to alkoxide.

The use of reactant concentrations when determining reaction order is an expedient, valid only if the activity coefficient of the species is invariant with concentration. Acidity functions, which are empirical scales that quantitate the activity of an acid or base as a function of concentration or solution composition have been determined for strongly basic solutions, including alkoxide/alcohol solutions [19]. The H_M function (Eq. (3)), in which pK_{SH} is the ionization constant for a weak acid (SH) in methanol and γ represents an activity coefficient, provides a measure of the ability of methoxide to abstract a proton from a neutral species in methanol solution.

$$(3) \quad H_M = -\log_{10}(a_{H^+} \gamma_{S^-} / \gamma_{SH}) = pK_{SH} + \log_{10}([S^-] / [SH])$$

Such scales are constructed by measuring the ratio $[S^-]/[SH]$, usually spectrophotometrically, and combining with the appropriate value of K_{SH} . The relationship between H_M and methoxide activity is more clearly demonstrated when the substitution:

$$a_{H^+} = K_M a_{MeOH} / a_{MeO^-}$$

in which K_M is the equilibrium constant for autoprotolysis of methanol, is made in Eq. (3) to give:

$$(4) \quad H_M = \log_{10}(a_{MeO^-}) - \log_{10}(a_{MeOH} K_M) - \log_{10}(y_{S^-}/y_{SH})$$

The relationship between H_M and the pseudo first-order rate constant (k_{obs}) for an S_N^2 reaction, represented by Eq. (5) is given by Eq. (6), in which y_{\ddagger} is the activity coefficient of the transition state (\ddagger) in the rate determining step [19]. In this analysis, the attainment of the equilibrium in Eq. (5) is assumed to be rapid and to favor the reactants.



$$(6) \quad \log_{10} k_{obs} = \log_{10}(k_0 K_M) + H_M + \log_{10}\{(a_{MeOH} y_{RX} y_{S^-}) / (y_{SH} y_{\ddagger})\}$$

Thus, provided the activity coefficient term in equation 6 is independent of methoxide concentration, a linear correlation between $\log(k_{obs})$ and H_M , with unit slope will result.

Linear correlations of $\log_{10}(k_{obs})$ for nucleophilic substitution at carbon with H_M have been reported, although slopes are less than the predicted value of 1 [20]. The variation in the slope was interpreted as a function of the difference in the solvation of RX and \ddagger compared to that for the indicator/conjugate base pair used to construct the H_M scale. $\log(k_{obs})$ for the reaction of DEMP with methoxide exhibits a linear dependence upon H_M , with a slope of 0.88 (Fig. 5(a)). We use the H_M function constructed from equilibria for the deprotonation of substituted aniline and diphenylamine indicators [21] in this work, after correction for the incorrect value of K_M used in its

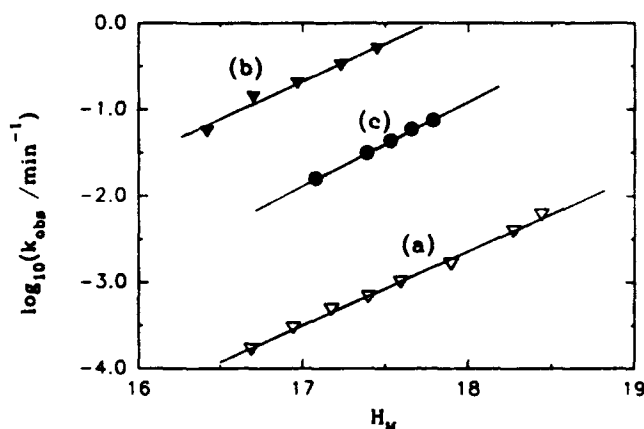


Figure 5. $\log_{10}(k_{obs})$ vs. H_M for reaction of: (a) DEMP with NaOMe (least squares gradient = 0.876, corr. coeff. = 0.998); (b) Ethyl benzoate with NaOMe (gradient = 0.857, corr. coeff. = 0.988); and (c) DMMP with NaOEt (gradient = 0.963, corr. coeff. = 0.999).

original calculation [19]. The linear relationship between $\log_{10}(k_{\text{obs}})$ and H_M for the DEMP/methoxide reaction, with its near unit gradient clearly demonstrates that nucleophilic displacement at phosphorus by methoxide is first-order with respect to methoxide. This interpretation is supported by rate data obtained for the alcoholysis of ethyl benzoate in sodium methoxide/methanol solutions (Table III). The B_{AC}^2 mechanism is well established for base catalysed substitutions at carbonyl centres, and the reaction is first order with respect to methoxide [22]. A plot of $\log_{10}(k_{\text{obs}})$ against H_M for the ethyl benzoate/methoxide reaction yields a straight line with a slope of 0.86 (Fig. 5(b)), which is virtually identical to the slope for the DEMP/methoxide reaction.

Values for H_E , the acidity function for ethoxide/ethanol solutions analogous to H_M , have not been reported, hence the relationship between $\log_{10}(k_{\text{obs}})$ and H_E cannot be established. However, the limited data available for ethanoxide/ethanol acidity functions indicate that the concentration dependence of ethoxide activity is similar to that of methoxide [23–25]. At the same concentration of alkoxide, the acidity function for ethoxide in ethanol is 2.1 to 2.2 units greater than that of methoxide in methanol [23]. A plot of $\log_{10}(k_{\text{obs}})$ for the reaction of DMMP with ethoxide vs. H_M (i.e., the methoxide activity scale) should be linear with unit gradient if the reaction is first order with respect to ethoxide provided H_E and H_M exhibit a similar concentration dependence. The plot of our data for this reaction exhibits a linear relationship between $\log_{10}(k_{\text{obs}})$ and H_M with a gradient of 0.96 (Fig. 5(c)) confirming the first order dependency of the reaction upon ethoxide. Thus, nucleophilic substitution of dialkyl methylphosphonates in alcohol solutions by alkoxides has been shown to be first order with respect to the nucleophile.

Conclusions

Despite the linear correlations between k_{obs} and $[\text{alkoxide}]^2$ obtained for reactions of DEMP with sodium methoxide and DMMP with sodium ethoxide at $[\text{alkoxide}]$ less than 1.5 M, these reactions do not involve 2 equivalents of alkoxide in the rate determining step. For both reactions, the rates have been shown to be linearly dependent upon the activity of the alkoxide, as represented by an appropriate acidity function. There is therefore, no requirement to invoke the involvement of hexacoordinate species to explain the high order dependency of the reactions upon alkoxide concentration.

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